CHEMICAL AND BIOLOGICAL EVALUATION OF OILS AND TARS PRODUCED UNDER VARYING COAL DEVOLATILIZATION CONDITIONS

Vassilis C. Stamoudis

Geochemistry Section
Energy and Environmental Systems Division
Argonne National Laboratory
Argonne, IL 60439

INTRODUCTION

Oils and tars are among the major coal-gasification by-products having potentially adverse health and environmental consequences. The production of oils and tars during gasification, pyrolysis, and hydropyrolysis is related to the initial coal devolatilization reactions. The yield has been shown to vary with temperature, pressure, residence time, gas/solid contact, gaseous environment, and presence of catalytic surfaces. Further, coal-gasification oils and tars have been shown to contain toxic chemicals, including polynuclear aromatic amines and hydrocarbons [1-4]. A comprehensive report of an extensive study relating process conditions to chemical and toxicological characteristics of coal-gasification oils and tars has been published [5]. A summary of some of the results and important findings is presented here.

EXPERIMENTAL

Experiments were conducted in a 2-lb/hr entrained-flow reactor operated by the Mellon Institute, in close cooperation with Environmental Research and Technology, Inc. The samples were analyzed by Argonne National Laboratory. Forty-nine successful runs of the reactor covered the following conditions: (a) reactor temperatures = 600°C, 800°C, and 1000°C; (b) gas-phase residence times = 0.2 s and 1.3 s; (c) reactor pressures = 3 atm and 10 atm; (d) reactant gases = He, H_2, CO_2, and steam; and (e) coal types = lignite and subbituminous coal. The organic by-products were trapped by means of three successive traps, and the trapped condensates were combined in proportion to the amounts produced. The combined oil/tar samples were then analyzed for organic compounds using computer-controlled, fused-silica, capillary-column gas chromatography (GC) (Hewlett-Packard 5880A). The aromatic relative retention index (RRI) [5,6] and the concentration of each peak were calculated and printed using custom software. GC/mass spectrometry (GC/MS) was used as necessary to confirm that the correct name was assigned to each RRI.

The Ames mutagenicity of the heavy tar trap samples was measured using the Ames assay (Salmonella TA98 strain with S-9 activation) [5]. All process conditions and chemical and toxicological data were entered into a mainframe computer, where the data were analyzed with great ease and flexibility by applying statistical analysis routines (CMS/SAS).

RESULTS AND DISCUSSION

The chemical composition of the combined oil/tar samples (Fig. 1), varied considerably, but the samples consisted mainly of aromatic compounds of one to four rings (Fig. 2). Therefore, the combined oil/tar samples were monitored routinely by RRI-GC for 62 chemicals, mainly one- to four-ring aromatic hydrocarbons (ranging from benzene to chrysene), and certain phenols and naphthols, acetophenone, indole, benzothiophene, benzofurans, and dibenzofuran.

In general, the most important of the process variables affecting chemical composition and mutagenicity was temperature. As seen in Fig. 1, the 1000°C-run samples were simpler mixtures in which phenols were absent and the level of alkylation was much reduced (Fig. 3). The amount of chromatographable material in these samples was very high. The mutagenicity of the heavy tar trap samples from the 1000°C runs was moderate (Fig. 4). Because the 600°C-run mixtures were much more complex, an additional 44 chemicals were monitored for several of these samples. The amount of phenols was high, and more polar and higher molecular weight materials were present, making the amount of nonchromatographable material higher. However, the mutagenicity associated with the 600°C-run heavy tar trap samples was very low. The 800°C-run combined oil/tar samples had both of the above characteristics -- a clearly higher degree of alkylation, intermediate chromatographability, and high mutagenicity (Fig. 4).

CONCLUSIONS

The results of this study suggest that changes in coal devolatilization conditions can significantly alter the chemical composition and toxicological properties of by-product oils and tars. The results also emphasize the importance of computer-assisted chromatographic analysis and data handling. Further, information of this kind is very useful in helping managers and engineers to design and build energy efficient and environmentally acceptable coal-conversion facilities.

ACKNOWLEDGMENTS

This work was supported by the U.S. Department of Energy's Morgantown Energy Technology Center as part of its Surface Gasification Environmental Program.

REFERENCES

[1] Stamoudis, V.C., S. Bourne, D.A. Haugen, M.J. Peak, C.A. Reilly Jr., J.R. Stetter, and K. Wilzbach, *Chemical and Biological Characterization of High-Btu Gasification (The HYGAS Process), I: Chemical Characterization of Mutagenic Fractions*, in Coal Conversion and the Environment: Chemical, Biological, and Ecological Considerations, D.D. Mahlum, R.H. Gray, and W.D. Felix, eds., U.S. Department of Energy, CONF-80-1039, pp. 67-95 (1981).

[2] Stamoudis, V.C., D.A. Haugen, M.J. Peak, and K.E. Wilzbach, *Bio-Directed Chemical Characterization of Condensates from Synfuel Processes*, in Advanced Techniques in Synthetic Fuel Analysis, C.W. Wright, W.C. Weimer, and W.D. Felix, eds., U.S. Department of Energy, CONF-81-1160 (PNL-SA-11552), pp. 201-214 (1983).

[3] Haugen, D.A., M.J. Peak, K.M. Suhrbier, and V.C. Stamoudis, *Isolation of Mutagenic Aromatic Amines from a Coal-Conversion Oil by Cation-Exchange Chromatography*, Analytical Chemistry, 54:32-37 (1982).

[4] Haugen, D.A., V.C. Stamoudis, M.J. Peak, and A.S. Boparai, *Isolation of Mutagenic Polycyclic Aromatic Hydrocarbons from Tar Produced during Coal Gasification*, in Polynuclear Aromatic Hydrocarbons: Formation, Metabolism, and Measurement, M. Cook and A.J. Dennis, eds., Battelle Press, Columbus, Ohio, pp. 607-620 (1983).

[5] Fillo, J.P., V.C. Stamoudis, J.R. Stetter, and S.W. Vance, *Influence of Coal Devolatilization Conditions on the Yield, Chemistry, and Toxicology of By-Product Oils and Tars*, U.S. Department of Energy, DOE/ET-14746-11 (ANL/SER-2), 243 pp. (1983).

[6] Stamoudis, V.C., *A Gas Chromatographic Scheme, Based on Relative Retention Indices, for Rapid Quantitative and Qualitative Analysis*, Pittsburgh Conf. on Analytical Chemistry and Applied Spectroscopy, Atlantic City, N.J., Paper No. 72, (March 1982).

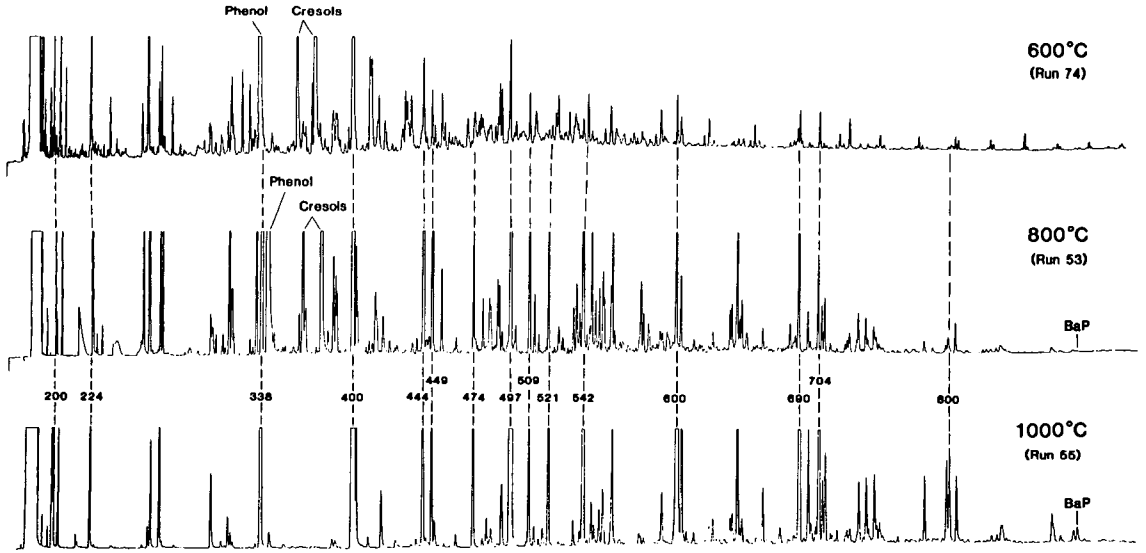

FIGURE 1 Typical GC Chromatograms for Combined Oil/Tar Samples Produced at 600°C, 800°C, and 1000°C (Peaks are labeled with the RRI: 200, benzene; 224, toluene; 338, Indene; 400, naphthalene; 444, 2-methylnaphthalene; 449, 1-methylnaphthalene; 474, biphenyl; 497, acenaphthylene; 509, acenaphthene; 521, dibenzofuran; 542, fluorene; 600, phenanthrene; 690, fluoranthene; 704, pyrene; 800, chrysene; BaP, benz[a]pyrene. GC conditions: 50 m x 0.23 mm OV-101 fused-silica capillary column from Hewlett-Packard; initial oven temperature (20°C for 2 min) raised to 270°C at 2°C/min and held at 270°C for 20 min; splitless injection; He carrier gas)

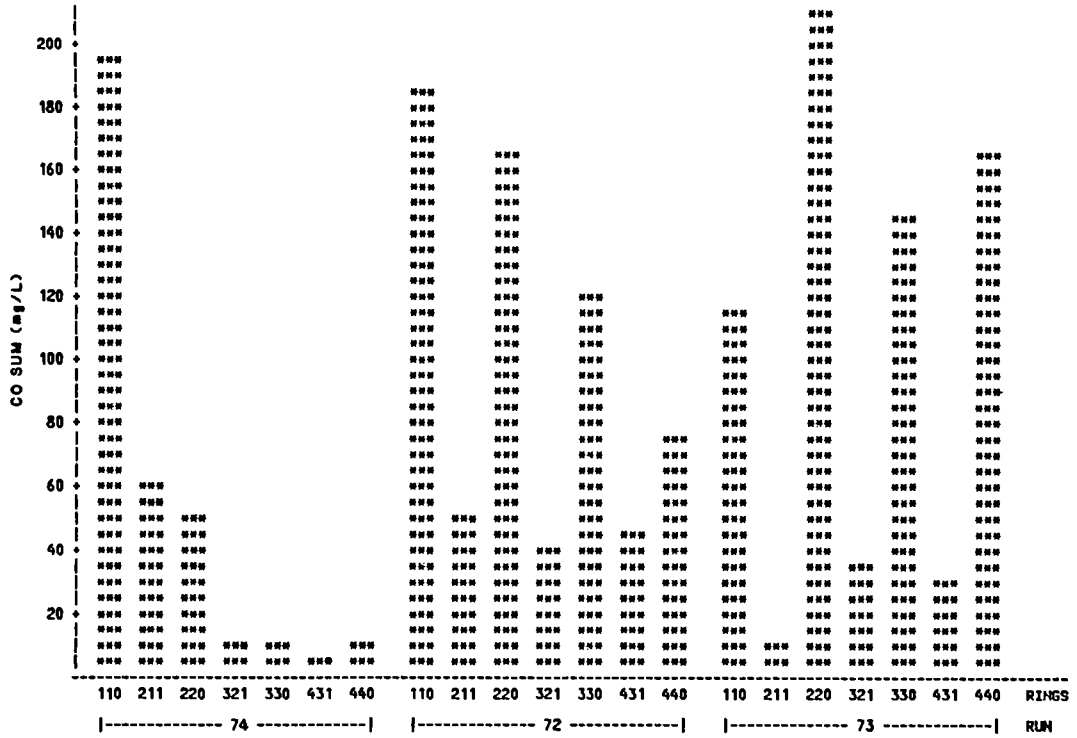

FIGURE 2 Analysis of Total Chromatographable Organics in Combined Oil/Tar Samples Versus Ring Structure for Reactor Runs 74 (600°C), 72 (800°C), and 73 (1000°C) (in the three-digit ring index, first digit = total number of rings, second digit = number of aromatic rings, and third digit = number of alicyclic rings)

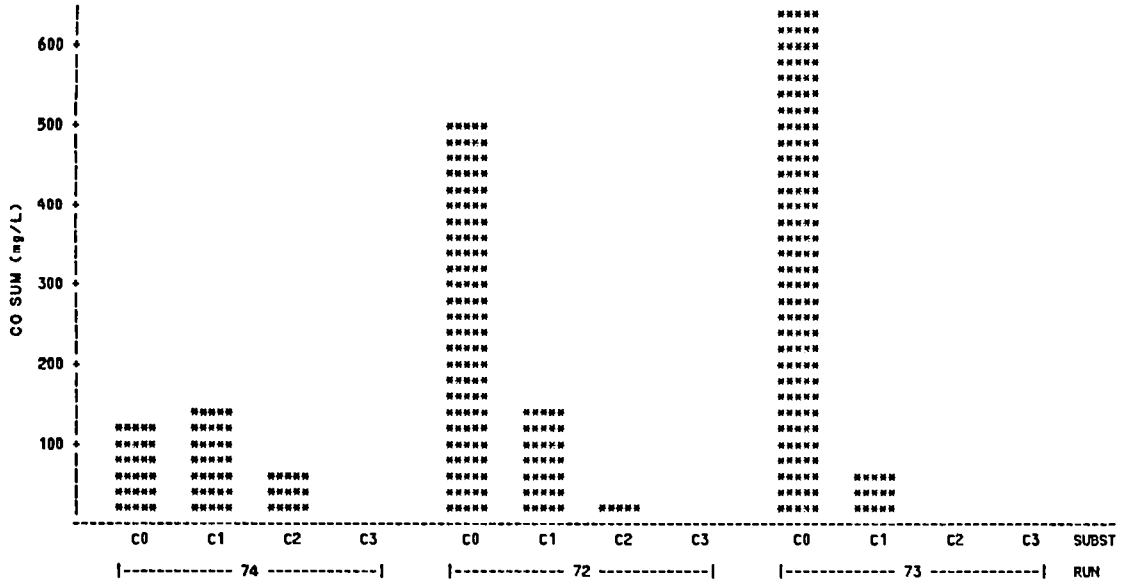

FIGURE 3 Analysis of Total Chromatographable Organics in Combined Oil/Tar Samples Versus Alkyl Substitution for Reactor Runs 74 (600°C), 72 (800°C), and 73 (1000°C)

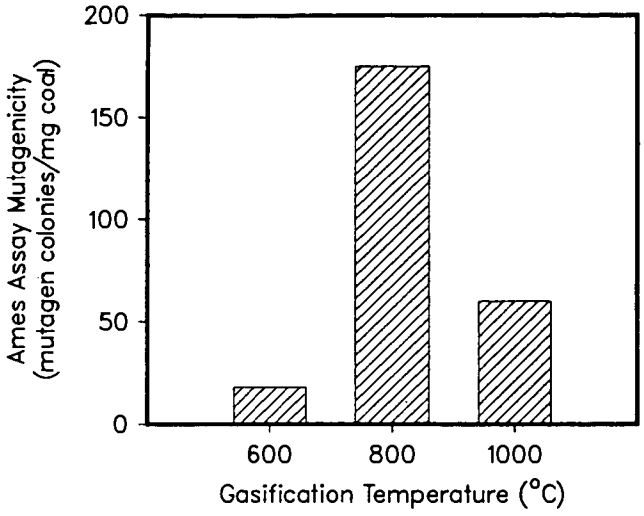

FIGURE 4 Mutagen Formation in Coal Devolatilization (calculated from dose response mutagenicity measurements)